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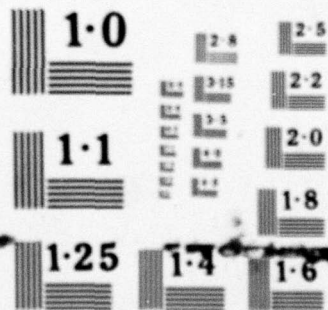
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The Reaction of Acetylene with Ni(100) and Ni(110) Surface at Room
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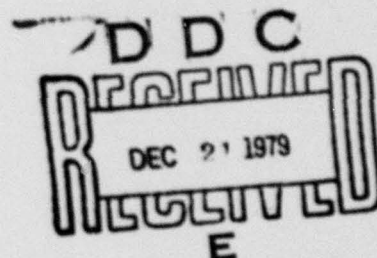
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The Reaction of Acetylene with Ni(100) and Ni(110) Surfaces at Room Temperature.*

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ABSTRACT: Ultraviolet photoemission spectroscopy using $h\nu=21.2\text{eV}$ and filtered 40.8eV radiation as well as temperature programmed thermal desorption spectroscopy are used to investigate the chemical reaction of acetylene with Ni(100) and Ni(110) surfaces at room temperature. Striking crystallographic effects and several coexisting phases are observed and found to be coverage and temperature dependent. A methodology is described and used to predict the relative energy levels for a variety of adsorbed hydrocarbon fragments on Ni surfaces. Such levels together with the thermal desorption spectra are used to identify the observed species. In particular, CH and CCH species are isolated on Ni(100) and Ni(110) surfaces, respectively, via low temperature adsorption and subsequent pulsed sample warming experiments. The room temperature adsorption phases are deduced using these ionization levels together with those of chemisorbed acetylene, atomic hydrogen and carbon. At room temperature on Ni(100) H, C, CH and C_2H_2 species form together below 2 Langmuirs exposure while CH species form thereafter, up to saturation exposure of ~ 10 Langmuirs. On Ni(110), H and CCH species form below 1.5 Langmuirs exposure followed by the formation of CH_2 and likely CH species. The relative stabilities of these species at elevated temperatures is: $\text{C}_2\text{H}_2 < \text{C}_2\text{H} \leq \text{CH} < \text{CH}_2$. A model for the bonding of acetylene and its reaction to form CCH species on Ni(110) is proposed.

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The ability of UV photoemission spectroscopy to provide chemically specific information about adsorbed species has made it a useful tool for surface chemistry. The ionization levels of adsorbed species can in many cases be directly related to those of free molecules so as to allow an assignment of the adsorbed species [1-2]. In cases where new molecular species form such an identification it is not possible and some other method of identification must be used. The relative energy levels calculated for various proposed species have previously been used to help identify new surface species [3-4]. Of particular relevance to this work was the identification of a CH species formed on a "chemically modified" Ni(111) surface [3]. This identification was later confirmed by high resolution electron energy loss studies of the vibrations of this new surface species [5].

In this work, we present photoemission studies of the reaction of acetylene with (100) and (110) nickel surfaces at room temperature. Together with our earlier studies of Ni(111) [3,5] we hope to better understand crystallographic effects in the reaction of acetylene with Ni. We also present in detail the methodology we use to predict the relative valence orbital energy levels of many possible simple hydrocarbon species such as CC, CH, CH₂, CCH and CCH₂. These levels together with thermal desorption mass spectroscopy are used to elucidate the nature of the acetylene derived species. We find that the reaction of acetylene on Ni(100) and (110) produces several new species which we can identify as simple hydrocarbon fragments. In particular, using low coverage, low temperature adsorption combined with momentary thermal processing, we isolate CH species on Ni(100) and CCH species on Ni(110). We find that at room temperature and low exposures on Ni(100) and Ni(110) several adsorbed species form concurrently: molecular acetylene, atomic carbon and hydrogen and CH species form on Ni(100) while hydrogen, chemisorbed acetylene and CCH species form on Ni(110). For higher exposures at room temperature we observe the formation of CH species on Ni(100) and CH₂ and possibly CH species on Ni(110).

II. Experimental Procedures:

The vacuum chamber is turbomolecular pumped with a freon cooled titanium sublimator and baffle. Typical operating pressures of 1×10^{-10} Torr were routinely obtained. As described elsewhere the experimental chamber contains facilities for in-situ LEED, AES, UPS and mass spectroscopy studies [3]. All photoemission studies were performed with an angle-integrating cylindrical mirror analyzer (CMA) and a D.C. resonance lamp. These measurements were done at two different time periods between which modifications were made to our resonance lamp so as to achieve higher intensities and permit filtered $h\nu=40.8$ eV studies [6].

The Ni(100) and (110) samples were prepared by conventional techniques [7] and mounted via .004 cm dia, 0.6 cm long Ta wire onto 1.5 mm dia. molybdenum leads of a multiple sample holder. This holder permitted each sample to be liquid nitrogen cooled to $T \sim 100\text{K}$ or resistively heated to $T \sim 1400\text{K}$ as measured with a chromel-alumel thermocouple spot welded to the back of each crystal. The Ni(111) sample used in our previous study [3,5] remained on our manipulator so as to enable comparative in-situ studies of all three principle low index faces of Ni.

All samples were cleaned by mild oxidation treatments, argon ion-sputtering and subsequent annealing [3,7]. Characterization of the clean surface was performed by LEED, Auger and photoemission analysis. Purified Matheson acetylene ($>99.6\%$) was used and examined for other impurities mass spectroscopically. Characterization of the LEED patterns upon acetylene adsorption and reaction was not undertaken for the (110) and (100) samples. The pressures and exposures cited here are uncorrected ion guage readings, and due to the location of the sample and ion guage within the chamber, these pressure readings may likely be slightly higher than at the sample. (As a calibration point we find that a 3L exposure of acetylene to Ni(111) forms a $p(2 \times 2)$ LEED pattern which ideally corresponds to a quarter monolayer coverage ($\sim 8 \times 10^{14}$ molecules/cm²).

Temperature programmed thermal desorption (TPTD) mass spectroscopy was performed with a quadrupole mass spectrometer located $\sim 3''$ away and in line of sight to the sample. Both the individual products as a function of temperature and the total desorption products were recorded - the latter using a storage scope and a fast repetitive scan mode of the spectrometer. Since hydrogen was the dominant product liberated after sub-monolayer exposures, we generally restricted ourselves to monitoring it alone. (Our multi-mass sample and hold method of following several desorption mass simultaneously [8] was therefore not used). The sample heating rates used were 10-15 K/sec.

The geometry of our photoemission measurements as well as the conditions of our d.c. resonance lamp at the two different times are the same as those reported elsewhere [4]. Again, we see that changes in the sample orientation produce small modifications in relative intensities of the ionization features - expected due to angular and polarization-dependent effects. In one case to be mentioned later, a very broad ionization feature shows slightly different peak positions for $h\nu=21.2$ and 40.8eV. We associate this effect with two overlapping ionization levels which have different frequency dependencies. We note that in most cases of doing $h\nu=40.8$ eV studies the orbital ionization intensities were so weak that saturation coverages of the adsorption/reaction process were only studied. Thus, coverage dependent studies at $h\nu=21.2$ eV were primarily used to separate and distinguish between the various phases.

III. The Identification of Hydrocarbon Species.

In two previous papers we have discussed identifying particular surface species from their observed energy levels. This has involved using comparisons to analogous gaseous molecules [3] as well as to Li or Be substituted homologous [3,4], free radicals [4] and model calculations of bound fragments on a nickel cluster [3,9]. In all cases these calculations do not explicitly take account of final state effects so that any comparison to experiment must be made on a

relative basis. Namely, the relative experimental level positions of known and unknown species are compared to the relative levels of calculated species. In this manner of comparison we avoid having to quantitatively predict I.P.'s. When one considers the many efforts to accurately calculate the ionization levels of CO on metal surfaces [10-13], one realizes the difficulties of doing similar calculations for hydrocarbon species. In the following discussion we summarize the method we use here to predict the relative level positions for a variety of simple hydrocarbon fragments. These results will be used later as a guide to help understand our photoemission results.

In Fig. 1 we show the measured ionization levels for acetylene [6,14] and some representative calculations of the ground state one electron energies and the ionization levels. Anderson has used an Extended Hückel approach modified to include two body repulsions to determine the lowest energy, geometric configuration of organometallics and adsorbed species [15]. The energy levels calculated for free acetylene with his method are indicated in b) and show some variance with the observed ionization levels shown in a). This is also true for more rigorous ab-initio LCAO SCF methods shown in c) and d). The levels in c) were calculated with an unrestricted Hartree-Fock method using a 4-31G basis set (Gaussian G-70 [16]). The levels in d) are the Hartree-Fock limit values of Clementi [18]. The ionization levels shown in e) were calculated by Cederbaum and Domcke [18] and agree very favorably with experiment.

In the analysis we do here we choose to combine the results of an Extended Hückel calculation which can simulate the bonding properties to a Ni surface [15] with the results of our Gaussian-70 calculations which describe the relative energy levels for free hydrocarbon molecules very well [19]. Thus, we try to use both methods in a complementary fashion so as to take advantage of each. The combined results are then used to guide the interpretation of our experimental results. In Figure 2 we present an example to show how this is done. Panel A shows the Extended Hückel calculations for free acetylene, free CH_2 fragments and three of these same fragments adsorbed in the bridging sites of a 31 atom Ni atom cluster. The 31

atom Ni cluster has 19 closed packed atoms on one (top) surface and 12 atoms below so as to simulate a (111) Ni surface. This cluster is displayed elsewhere [15]. (We note that the "free" CH_2 levels are also identical to those determined by moving the three CH_2 species 10 Å away from the original surface cluster.) From these calculations we learn how certain levels are shifted upon bonding to the Ni surface and where all levels lie relative to those of free acetylene. Although differences in bonding sites slightly alter the locations of some levels, this is a small effect considering the levels of accuracy of this method and the manner in which we hope to use these levels. Bond site effects are further known to be small for the case of CO bonded to transition metal surfaces or in the carbonyls [20].

In panel B we make a similar comparison of the levels for free C_2H_2 and CH_2 using the Gaussian-70 program [16]. Based upon the relative level shifts observed in panel A upon bonding to Ni we can predict what the pattern of levels should look like on Ni. The use of the levels from this ab-initio method serves to provide us with a better description of the relative level spacings between both the higher lying σ -valence levels of CH_2 and the carbon $2s\text{s}-2s\text{s}^*$ levels whereas the "renormalization" of these levels by the Extended Hückel method takes into account substrate screening and bonding effects. Finally, we compare the relative calculated levels for free acetylene and the expected levels for CH_2 on Ni (111), panel B, to the measured ionization levels of acetylene, panel C, and predict where the ionization levels of a CH_2 species on Ni should lie. Here, the relative positions of the CH_2 σ -levels and carbon $2s\text{s}$ levels are essentially derived from panel B modulo any bonding shifts found in A, while the absolute location of the lowest lying carbon $2s\text{s}$ level relative to acetylene is derived from panel A. The latter is done to account for charge transfer and any differential screening effects which may occur in the presence of nickel surface atoms. However, we note that the large "relaxation / screening shift" occurring for chemisorbed acetylene [1] may not occur for the other chemisorbed fragments and will alter our predicted I.P.s. To zeroth order we expect these differential shifts to be less for these fragments which may shift all levels upward by as much as 1.5eV

relative to the levels of acetylene. Thus, the scale for our predicted I.P.'s is uncertain by this amount.

Following the forementioned procedure we show in Fig. 3 the molecular orbital energies for a variety of simple hydrocarbon species, all displayed relative to the molecular orbital energies of acetylene calculated with the Gaussian-70 program [16]. The dashed levels indicate orbitals of mixed parentage and whose locations are more susceptible to error. We note in comparing these predicted levels, that some species are difficult to distinguish, eg CH and CH₂. Other species such as C and C₂ have markedly different energy levels and can be easily distinguished. In several cases we find that the different states of hydrogen desorbing from the surface during TPTD provides additional help in distinguishing between some of these species as will be discussed later.

IV. Experimental Results

In Fig. 4, we show the $h\nu=21.2\text{eV}$ photoemission spectra, $N(E)$, for two different exposures of acetylene to Ni(100) at room temperature. The difference spectra, $\Delta N(E)$, displayed in panel a) shows a coverage dependence to the adsorption process which is suggestive of multiple phase formation. For exposures above ~ 2 Langmuirs (2L) the additional features in the difference spectra are similar to those seen for higher exposures of acetylene to Ni(111). Here, we believe that the broad peak centered at 7.6 eV consists of two peaks split by about $1/2$ eV and show further evidence for this latter. Since our TPTD results (to be discussed later) indicate that this species is a hydrocarbon, we therefore designate it as C_XH_Y . For exposures below 2L the features in $\Delta N(E)$ are more complex and can be associated with the levels of chemisorbed acetylene, a carbon species, and some of the forementioned C_XH_Y phase. In panel b) we show the difference spectra taken with filtered $h\nu=40.8\text{eV}$ radiation at saturation coverages. We indicate the levels of chemisorbed acetylene on Ni(100) [8] and the levels for the C_XH_Y species. Here the levels for the C_XH_Y species were determined from the

$h\nu=21.2\text{eV}$ results in panel a) and the low temperature studies to be described later. The sum of these two sets of levels produce level positions and relative level intensities similar to those observed in b) except for two peaks at ~ 13 and 4eV . These peaks are identical to those of a C_X species which we form by heating to 650K to decompose the adsorbed hydrocarbon species and desorb all hydrogen from the surface (as shown in panel c). Evidently some C_X species form at room temperature initially during the 2L exposure as evidenced by the peak in the $h\nu=21.2\text{eV}$ spectrum at $\sim 4\text{eV}$ in Panel B. Thus, we can identify C_2H_2 , C_X , and C_XH_Y species formed together on $\text{Ni}(100)$ at room temperature below 2L exposure and predominantly C_XH_Y species above.

We can more clearly isolate the C_XH_Y species by performing the acetylene adsorption at low temperatures followed by momentary heating of the sample to higher temperatures. In Fig. 5 we show the photoemission results at $h\nu=21.2$ and 40.8eV for a 2L exposure of acetylene to $\text{Ni}(100)$ at $T\sim 100\text{K}$, followed by momentarily heating the sample to 425K . The difference spectra after thermal conversion shows both a C_XH_Y and a C_X species. For low temperature exposures above 2L longer heating and/or higher temperatures are needed to completely convert chemisorbed C_2H_2 to the other species. These results suggest that chemisorbed acetylene on $\text{Ni}(100)$ is more stable at higher coverages in the presence of these other species. For a 1L exposure, the lowest exposure studied at low temperatures, we observe that C_2H_2 partially converts to C_XH_Y species after warming to about room temperatures. The C_X species then form at higher temperatures above room temperature. We cannot determine whether these C_X species are derived from C_2H_2 or C_XH_Y . At higher temperatures (and at low/high coverages) after all C_2H_2 disappears, the C_XH_Y species decomposes to produce more C_X species.

In Fig. 6 we show our photoemission results for the room temperature adsorption of acetylene on $\text{Ni}(110)$. For higher exposures at $h\nu=21.2\text{eV}$, shown in panel a, we see a valence level structure somewhat similar to that observed on $\text{Ni}(100)$. Again, this broad peak can be

resolved into several distinct components from the high and low coverage difference spectra shown in panel b. At the lowest coverages (1.5L) we observe an increase in the work function of 0.1 eV and hydrogen desorption features (to be discussed) which are characteristic of chemisorbed hydrogen on the surface. The presence of adsorbed atomic hydrogen chemisorbed on Ni(110) produces a weak broad peak at 5.8eV below E_F as observed on Ni(111) [21,22]. We can attribute the broad peak between 4-6 eV in the 1.5L $\Delta N(E)$ spectra with adsorbed hydrogen. The remaining peaks at 10.6 and 7.2 eV for this 1.5L exposure can be associated with another phase which we call C_XH_Y' and are able to also isolate from our low temperature studies (to be discussed). For exposures above 3L we observe two levels at 10.2 and 7.4eV characteristic of another hydrocarbon species which differ in location from those seen for CH on Ni(111) and C_XH_Y on Ni(100). We refer to this species as C_XH_Y'' . For exposures between 1.5-3L a level at ~ 9 eV and a skewing of the -11 eV level for C_XH_Y' to larger energies suggests the presence of some small amount of chemisorbed acetylene. The $h\nu=40.8$ eV spectra is shown in Fig. 6 panel c. Here we observe a broad almost structureless valence band between 11-6eV and a very broad band at 14-17eV in the carbon 2s orbital region. These broad levels are consistent with the superposition of the valence levels found for chemisorbed C_2H_2 on Ni(110) [26], C_XH_Y' and C_XH_Y'' species.

The levels shown for chemisorbed C_XH_Y' are again more clearly determined from our low temperature studies. In Fig. 7 we show the results of thermal processing of a 1L exposure of chemisorbed acetylene adsorbed on Ni(110) at $T \sim 100$ K. Momentary heating to room temperature produces a new phase with levels similar to those occurring for room temperature exposures below 3L. For higher initial coverages of chemisorbed acetylene at low temperatures (>1.5 L exposure), we find that warming to room temperature does not convert all the C_2H_2 to C_XH_Y' and that further warming to higher temperatures forms C_XH_Y'' . These C_XH_Y'' species must form from the excess unconverted chemisorbed acetylene and not from the C_XH_Y' species since we see no disappearance of C_XH_Y' as C_XH_Y'' forms.

The temperature programmed thermal desorption spectra as a function of exposure of acetylene to the (111), (100) and (110) nickel surfaces at room temperature are shown in Fig. 8. Since the decomposition of hydrocarbon fragments on Ni(111), (100) and (110) surfaces produce almost exclusively molecular hydrogen we show only hydrogen desorption spectra. These desorption spectra are not calibrated and indicate relative signals on each surface. From previous studies on Ni(111) [3,5] the hydrogen desorption occurring near 410K arises from the decomposition of chemisorbed acetylene while the desorption above ~430K arises from the decomposition of CH and above ~520K from CH₂ and possible polymerized species. The desorption spectra on Ni(100) show a coverage-dependent desorption peak between 400 - 430 K and higher temperature features (above 450K) similar to those observed on Ni(111). On Ni(100) there also appears to be some hydrogen desorption on the leading edge of the 430K peak suggestive of small amounts of chemisorbed atomic hydrogen. This correlates to the formation of carbon on Ni(100) below 2L exposure as seen in Fig. 4.

For Ni(110) an atomic hydrogen desorption feature is evident at low acetylene exposures and represents ~1/2 of the total hydrogen desorption observed. We therefore postulate that at room temperature and up to 2L exposure, half the hydrogen in acetylene is removed and becomes bonded as atomic hydrogen to the Ni(110) surface. At higher exposures we see less atomic hydrogen and significantly more of the higher temperature hydrogen decomposition products. Our photoemission studies of the decomposition as a function of heating temperature indicate that the desorption features for acetylene on Ni(110) appear to be largely intrinsic to the initial adsorbed species and are not caused by the decomposition of the new hydrocarbon species formed at higher temperatures. Namely, we see C_XH_Y' and C_XH_Y'' species gradually disappear to form C_X as we incrementally pulse heat the sample to higher temperatures. The C_XH_Y'' species persists to the highest temperatures. We thereby relate the desorption features above ~450K (i.e., the peak at ~550K at saturation coverages) to the decomposition of the C_XH_Y'' species.

IV. Identification of the Observed Hydrocarbon Phases

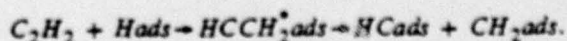
We have distinguished four species in our studies of acetylene on Ni(100) and (110) surfaces which we have labelled, as C_X , C_XH_Y , C_XH_Y' and C_XH_Y'' . These are in addition to the molecular adsorbed phases of acetylene formed on each face. In Table I we summarize the vertical ionization levels observed for chemisorbed acetylene and the various fragments observed on the Ni surfaces studied. In identifying these species we consider both the energy levels of Fig. 3 and our thermal desorption results. As discussed next, these new species can be identified as atomic carbon, CH, CH_2 and CCH species.

The C_X species has similar levels on each surface. This species has levels relative to chemisorbed acetylene which are characteristic of atomic carbon. We rule out C_2 species (or C_3 , C_4 , etc. species) since these would have $2\sigma_g$ and $2\sigma_u$ molecular orbitals formed from the bonding and antibonding combination of the carbon 2s atomic levels. Such differences in the lowest lying carbon 2s-derived levels clearly distinguish atomic carbon from any other carbon species (including a graphitic overlayer).

The C_XH_Y species formed on Ni(100) at room or low temperatures has similar high lying valence levels to those for the CH species on Ni(111). However, the position of the lower lying level differs by ~ 1 eV and suggests from Fig. 3 that C_XH_Y is a CH_2 species. Although such an assignment agrees with the formation of carbon on the surface at low coverages, we do not see any increase in surface carbon at higher exposures when more C_XH_Y forms. Thus, the carbon formed at lower exposures need not be a product of forming CH_2 from C_2H_2 . We thereby assign the C_XH_Y species to CH species and believe that the difference in location of the $2\sigma_g$ level relative to that found for CH on Ni(111), arises from differences in its bonding site, geometry and/or relaxation/screening effects on Ni(100). The similarities in the thermal desorption spectra on Ni(100) and Ni(111) above $T > 450$ K also support this conclusion.

The C_XH_Y' species formed on Ni(110) at low coverages and room temperatures has slightly different energy levels and work function changes from that occurring at higher coverages and liquid nitrogen temperatures. These differences may arise from small differences in bonding sites, molecular orientation on the surface or molecular geometries. Such differences may arise from differences in packing densities and the presence of coadsorbed acetylene at room temperature. In identifying the nature of C_XH_Y' we note that the similarity of these levels to chemisorbed acetylene might initially suggest a thermally activated change in acetylene bonding site on Ni(110). However, the thermal desorption results in Fig. 8 indicate that below $\sim 2L$ about half of the hydrogen atoms in acetylene have become dehydrogenated and bound to the surface. The dehydrogenated species in Fig. 3 which has levels consistent with those observed is a CCH species. We thereby associate the C_XH_Y' phase with a CCH species. From our thermal desorption results the CCH species decompose between $\sim 380-475^\circ K$. The second C_XH_Y'' phase on Ni(110) which forms at higher exposure has levels somewhat similar to the CH species on Ni(100) and Ni(110). However, the two higher lying levels of C_XH_Y are more greatly split than expected for a CH species [see Fig. 3] and the lowest lying level occurs at a lower energy. Both of these differences are expected for a CH_2 species. However, we must justify the absence of atomic carbon in forming CH_2 on Ni(110) from impinging acetylene.

The presence of atomic hydrogen on the surface from the low coverage reaction, $C_2H_2 \rightarrow CCH_{ads} + H_{ads}$ can provide another route to form CH_2 without producing carbon. The disappearance of atomic hydrogen from the surface for higher exposures as observed in Fig. 8, suggests its consumption in forming CH_2 . Given these constraints, we can postulate the following reaction of incident acetylene to form CH_2 :

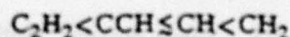


Here $HCCH_2^*$ is an unstable surface intermediate. The energy levels of a CH species as found on Ni(100) or Ni(111) would be masked by those for the CH_2 species. Indeed the additional

hydrogen desorption observed in Fig. 8 on Ni(110) which occurs above the 2L exposure at about 450-550K can be associated with the decomposition of CH species [3]. The CH₂ species decompose above 550K.

VI. Summary and Discussion

The reaction of acetylene with Ni(100) or Ni(110) surfaces at room temperature is strikingly more complex than observed on Ni(111) [3,5]. On Ni(111) it was found that acetylene chemisorbs molecularly to form a $p(2 \times 2)$ overlayer (3L exposure) after which CH species form. On Ni(100) we observe C, CH and C₂H₂ forming together at low coverages (< 2 L exposures) and CH species above. On Ni(110) H and CCH species first form (< 1.5 L exposures) together with trace amounts of chemisorbed acetylene (1.5 - 3.L exposures), followed by the formation of CH₂ and likely CH species (> 3L exposures). From our thermal desorption results we predict the following relative stabilities for the various hydrocarbon phases we observe:



We note that such relative stabilities apply under our experimental conditions. The presence of high hydrogen partial pressures or particular surface contaminants could alter this.

The multiple phase formation we observed here has not been found in other detailed studies on Pt(111) [4,23] but may also occur on Fe(100) [24] and Ir(100) [25] surfaces. One also clearly sees the need to observe all the valence ionization levels and consider other measurements combined with photoemission, such as thermal desorption studies, to help discriminate amongst the various possible species.

In general it is difficult to determine the microscopic details of the reaction of all these species. However, for the formation of CCH on Ni(110) from chemisorbed acetylene (at low temperatures) we propose an idealized model for the formation of CCH on Ni(110) from

chemisorbed acetylene. Using the molecular geometry for chemisorbed acetylene on Ni(110) at low temperatures [26] together with a proposed bonding model for acetylene on Ni(111) [27], we suggest in Fig. 9 a model for the bonding of acetylene to Ni(110). This bonding site is similar to the site for chemisorbed acetylene on Ni(111) and is also the bonding site for oxygen on Ni(110) [28]. This lower coordination bonding site on Ni(110) than on Ni(111) is also consistent with the weaker molecular distortions observed on Ni(110) than on Ni(111) [26]. In warming chemisorbed acetylene a CCH species may form when chemisorbed acetylene rocks about the two bridging Ni atoms and places a hydrogen atom of the molecule in close proximity to the nickel surface. The interaction of the hydrogen with the surface [29] as well as the interaction of one of the carbon atoms with several metal atoms may allow the removal of that hydrogen atom and the formation of a new carbon metal bond(s). The hydrogen atom removed also bonds to the surface (not shown in Fig. 9). The high coordination of CCH to Ni atoms in this new geometry may allow this to be a stable bonding configuration. However, the details of this final geometry or bonding configuration are unknown. As mentioned before, the CCH species which forms at room temperature in coexistence with chemisorbed C_2H_2 and hydrogen likely has a slightly different molecular orientation and surface geometry than the isolated high coverage phase we form by momentary thermal processing of chemisorbed acetylene.

Finally, we briefly compare our findings to those of other recent experiments on Ni. High resolution electron energy loss (HREEL) results have been obtained by Bertolini, et. al. [30] to characterize the saturation coverage phase of acetylene on Ni(100) at room temperature. With an experimental beam width at half maximum of $\sim 200 \text{ cm}^{-1}$, they observed peaks at 746, 988, 1330 and 3025 cm^{-1} . Based upon studies of adsorbed acetylene and CH species on Ni(111) [27,5] we believe these vibrational spectra on Ni(100) arise largely from the superposition of chemisorbed C_2H_2 and CH species on Ni(100). The adsorption of acetylene on a stepped Ni(111) surface [$5(111) \times (110)$] has also been examined by HREELS [31]. Such stepped surfaces may be related to the Ni(110) surface as both surfaces contain rows of low

coordination metal atoms. On the stepped surface of Ni the dehydrogenation of chemisorbed acetylene to form C_2 species was observed even at $T \sim 140K$. [31]. Also observed was considerable CH stretching vibrations when little CH or C_2H_2 species occurred. This we believe suggests the presence of CCH species as well. It is interesting that of all the nickel surface studied, acetylene only partially dehydrogenates on the more open (stepped-like) surfaces. Such dehydrogenation effects near steps may also be the result of sterically unhindered rotational motions of the molecule about the step which can position the molecule's carbon atoms into high coordination sites as proposed in our dehydrogenation model for C_2H_2 on Ni(110).

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Table I Summary of the observed vertical ionization levels for the various acetylene-derived phases observed on Ni(111), [refr. 3,5], Ni(100) and Ni(110) surfaces. Low temperature (LT), room temperature (RT), low coverage (LC) and high coverage (HC) conditions of formation are indicated where necessary.

SURFACE	PHASE	VERTICAL I.P. (in eV, $E_F=0$)			CHEMICAL ASSIGNMENT
Ni(111)					
	C_2H_2 LT/RT	16.8	11.3	9.1	molecular C_2H_2
	CH RT	{ 15.5	7.6 HeI 8.0 HeII	}	CH species
	C_x	12.9	4.2		atomic carbon
Ni(100)					
	C_2H_2 LT	16.8	11.0	8.7	molecular C_2H_2
	C_XH_Y LT or RT	{ 16.6	7.6 HeI 8.0 HeII	}	CH species
	C_x	12.7	4.2		atomic carbon
Ni(110)					
	C_2H_2 LT	16.4	11.2	8.7	molecular C_2H_2
	C_XH_Y' LC/RT HC/LT	(est 16.0-16.5) 16.0	10.6 10.2	7.2 7.4	CCH species
	C_XH_Y'' RT	(est 16.5-17)	9.0	7.5	
	C_x	12.6	4.3		atomic carbon

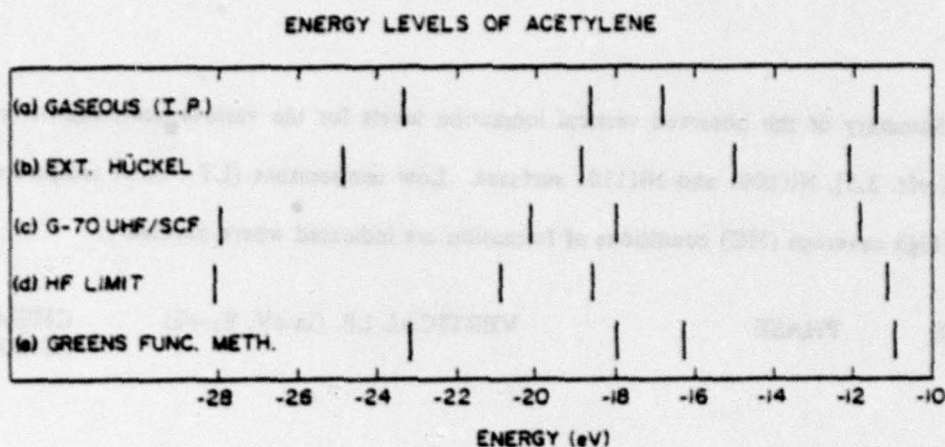


Figure 1.

Comparison of the gaseous vertical ionization levels of acetylene [6,14] (a) to the ground state orbital energies calculated with (b) an Extended Hückel method [15] and (c) an unrestricted Hartree Fock LCAO/SCF method [16] using a 4-31G basis. Near Hartree Fock limit levels [17] (d) and calculated vertical ionization potentials [18] (e) are also shown for comparison.

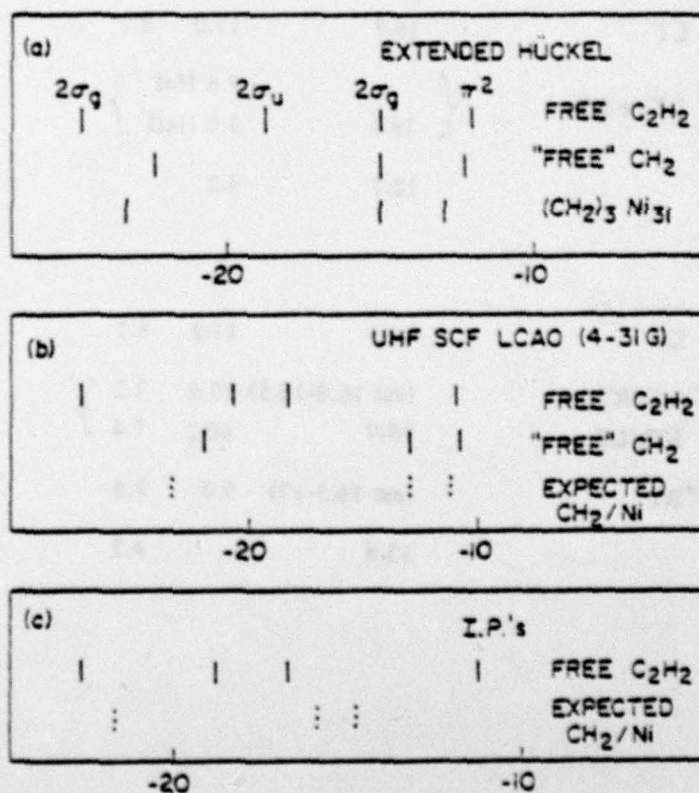


Figure 2.

Comparison of the relative molecular orbital energies calculated for acetylene and CH₂ species using an Extended Hückel method [15], panel A, and using a LCAO/SCF method [16]. From panels A and B we predict the I.P.'s for a CH₂ species on a Ni surface (panel C) as discussed in the text.

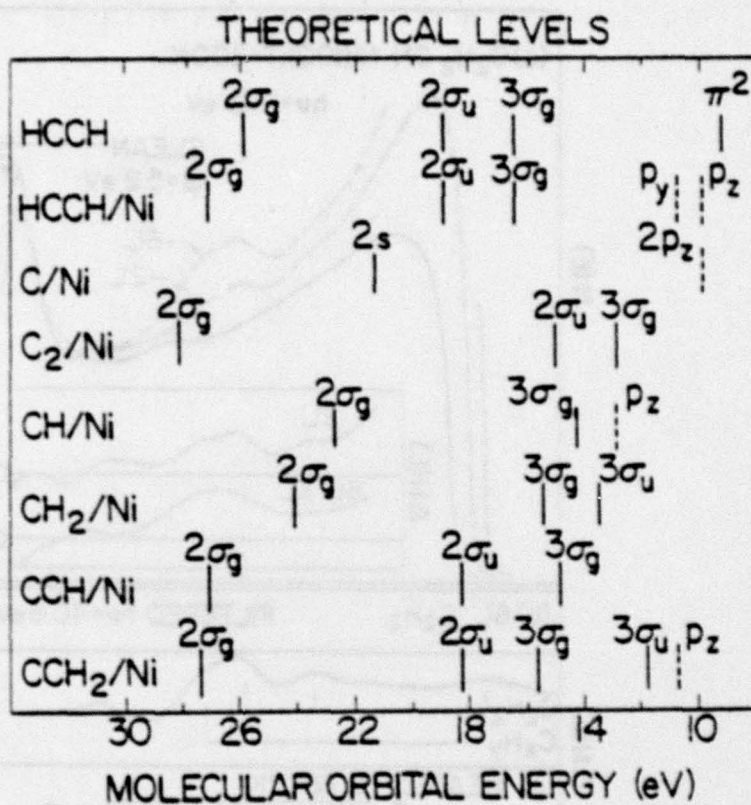


Figure 3

Predicted energy levels for various hydrocarbon species on Ni relative to the levels of acetylene as described in the text.

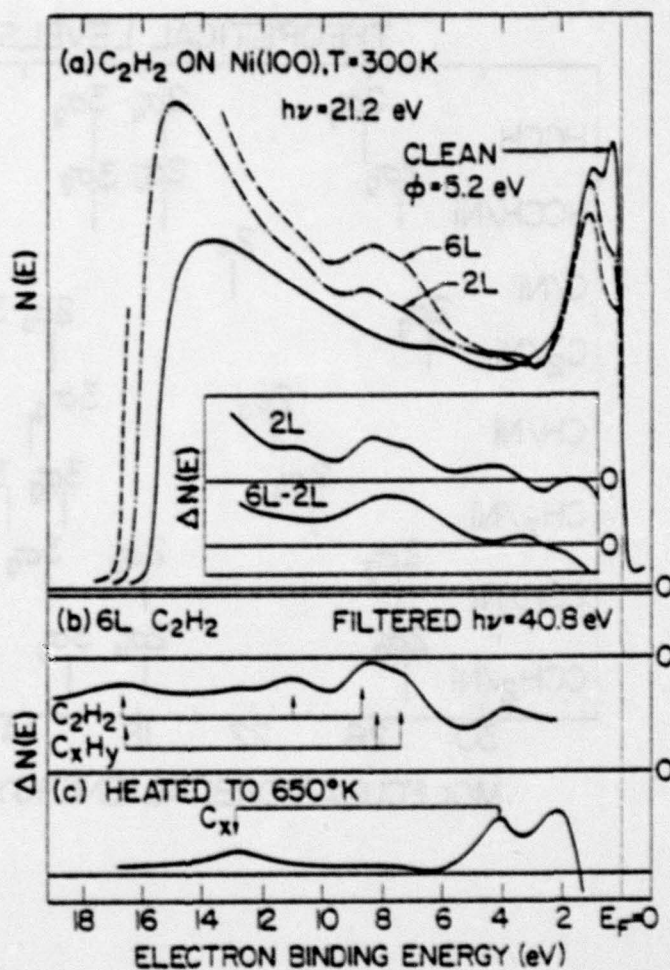


Figure 4.

U.V. photoemission energy distribution spectra $N(E)$ for clean $Ni(100)$ and for two different acetylene exposures (in Langmuirs) to $Ni(100)$ at room temperature, panel (a). The difference spectra, $\Delta N(E)$, obtained with filtered $h\nu = 40.8$ eV radiation before and after heating are shown in panels (b) and (c). The levels which can be associated with specific species are denoted (see text).

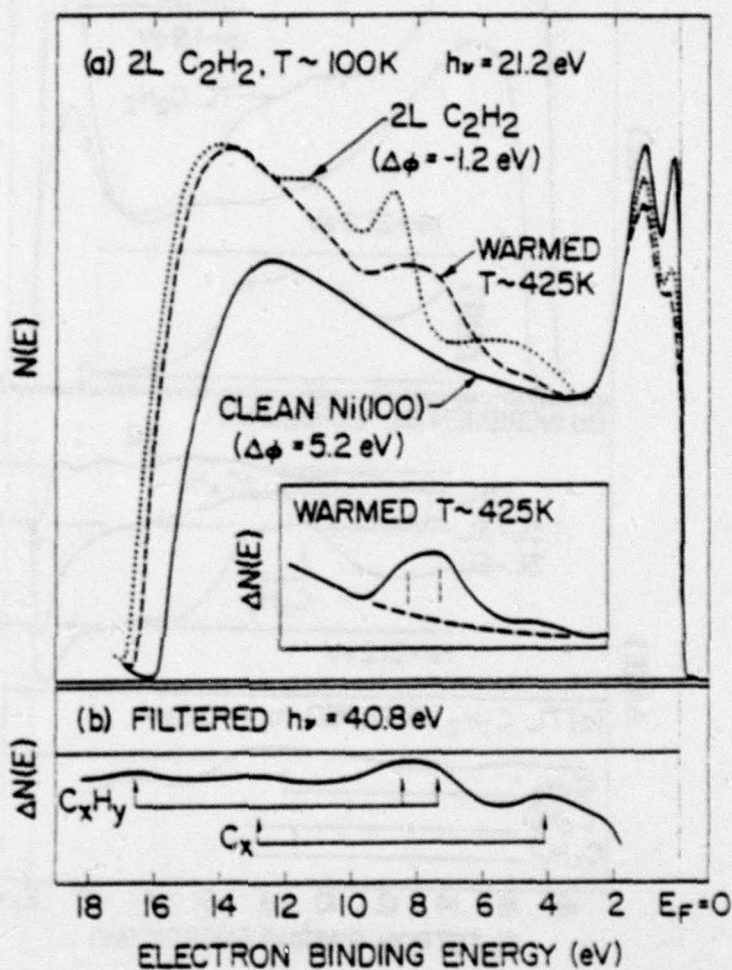


Figure 5.

U.V. Photoemission spectra, $N(E)$, for clean Ni(100) at $T \sim 100K$ and after exposure to 2 Langmuirs of acetylene at $T \sim 100K$, followed by heating to 425K, panel (a). The filtered $h\nu = 40.8 eV$ difference spectra $\Delta N(E)$, after the heat treatment is shown in (c). The levels which can be associated with specific species are denoted (see text).

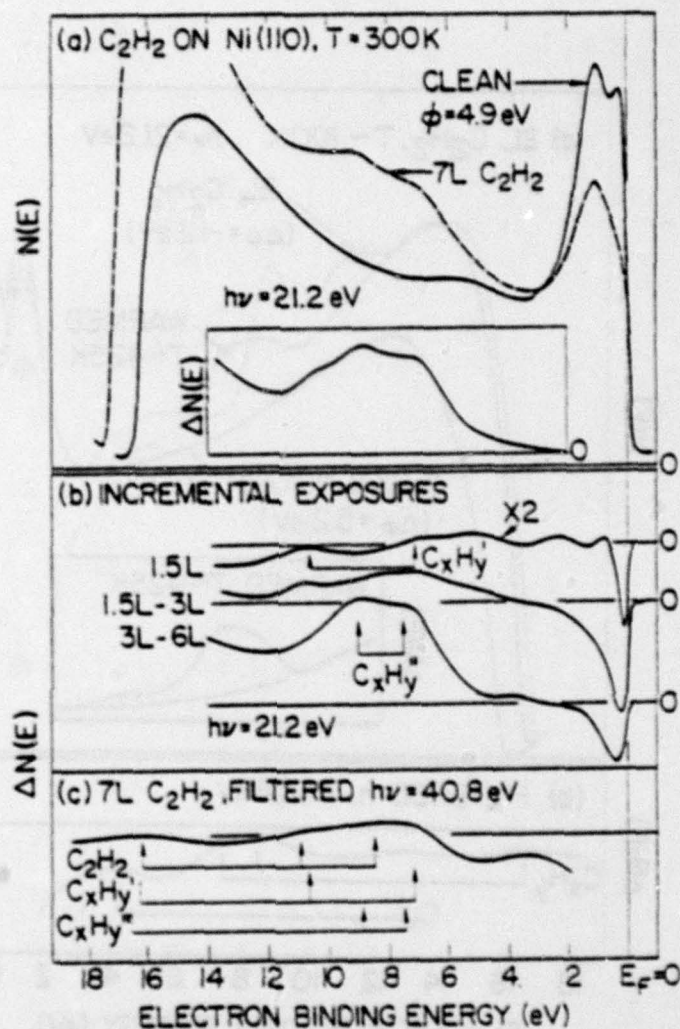


Figure 6.

U.V. Photoemission spectra, $N(E)$, for clean $Ni(110)$ at room temperature and after exposure to 7 Langmuirs of acetylene, panel (a). The difference spectra, $\Delta N(E)$, between various exposures are indicated in panel (b) while the filtered $h\nu = 40.8 eV$ $\Delta N(E)$ spectra is shown in panel (c). The levels which can be associated with specific species are denoted (see text).

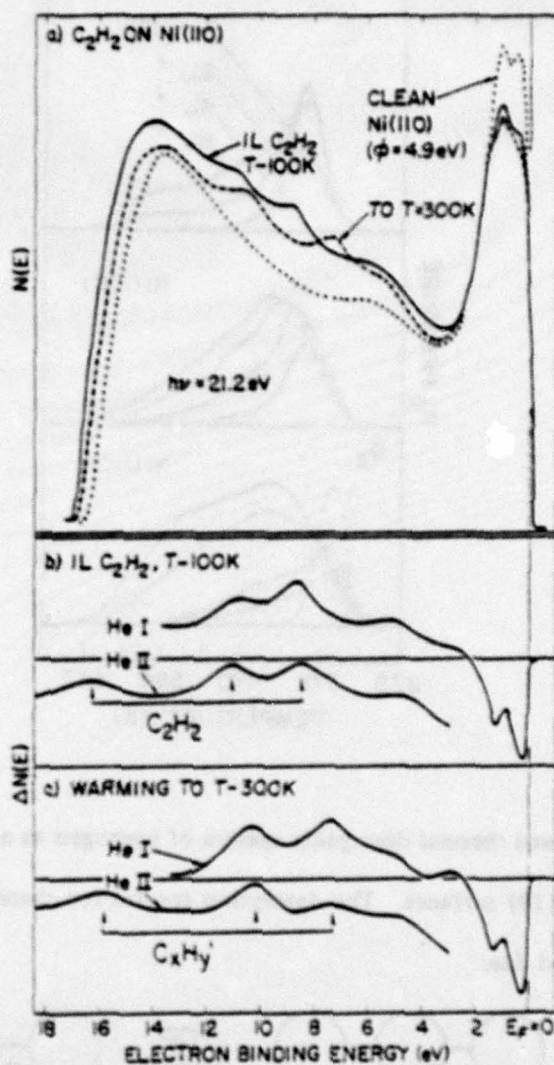


Figure 7.

U.V. Photoemission spectra, $N(E)$, for clean Ni(110) at $T \sim 100$ K, after exposure to 1 Langmuir of acetylene and followed by warming to $T \sim 300$ K, panel (a). The difference spectra for $h\nu = 21.2$ eV and $h\nu = 40.8$ eV are shown in panels (b) and (c) before and after conversion of chemisorbed acetylene.

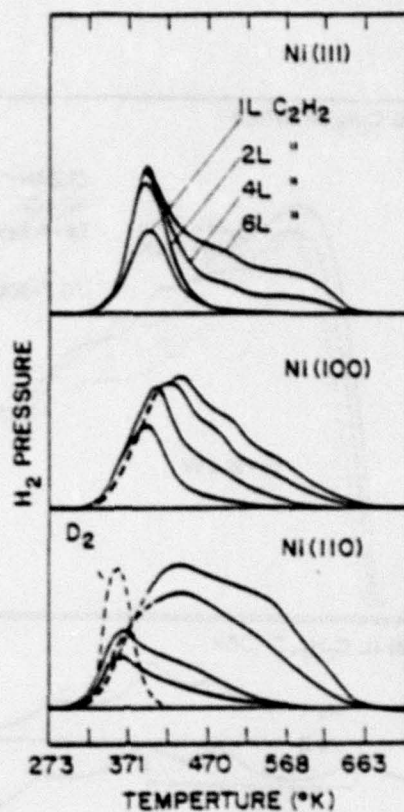


Figure 8.

Temperature programmed thermal desorption spectra of hydrogen as a function of acetylene exposure to Ni(111), (100) and (110) surfaces. The desorption spectra for chemisorbed hydrogen from Ni(110) is indicated by the dashed line.

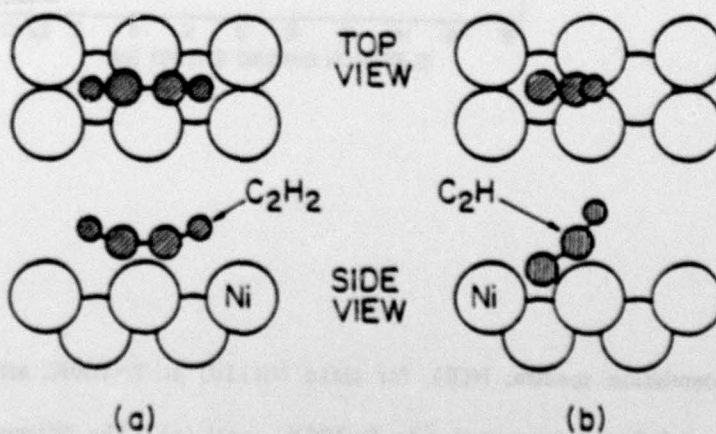


Figure 9.

Schematic model of the bonding and reaction of chemisorbed acetylene on Ni(110) to form CCH species as described in the text. The hydrogen atom produced in the reaction bonds to the surface at some unknown site and is not shown in (b).

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